



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

PRESSURE AS A FACTOR IN THE FORMATION OF ROCKS AND MINERALS

JOHN JOHNSTON

Geophysical Laboratory, Carnegie Institution of Washington

It is not surprising that application of the knowledge comprised in the older chemistry should have yielded comparatively little information as to the way in which rocks and minerals actually form; and for this reason. The older chemistry dealt in the main with the formation and behavior of substances at temperatures confined to a very small range and practically at a single pressure only—that of the atmosphere; in other words, it dealt with the merest slice of the surface which would represent the behavior of the substance throughout the range of temperature and pressure within which it is capable of existence. At the same time there was a failure to recognize that its work was so limited in character, and consequently the endeavor to deduce regularities from the behavior of substances at ordinary temperature and pressure—under arbitrary conditions, in other words—was but partially successful. The reason for this is clear if we consider how our ordinary chemistry—that of the 20° C. level—would be changed at the 200° level, for a large number of compounds would then have become unstable; and again, that the number of compounds persisting at the 1,000° level, and a fortiori at the 2,000° level, would be but a small fraction of those which exist at ordinary temperatures.

Igneous rocks and minerals have formed under conditions much removed from 20° and 1 atm. pressure; so that we are little likely to ascertain much about their formation except by thorough and extensive investigations over a wide range of temperatures and pressures, investigations which would at the same time throw much needed light on a number of very important chemical problems. Incidentally it may be observed that the variables temperature and pressure are completely analogous; that besides the ordinary freezing-point of a liquid—in stating which we imply a definite

pressure of 1 atm.—there is also the freezing-pressure at a definite temperature; for example, mercury freezes at -38.85° under 1 atm.; at 0° C. its freezing-pressure—the pressure which will cause it to freeze—is about 7,600 atm.

The purpose of the present paper is to discuss briefly the available experimental evidence in the light of the principles involved, to indicate the conclusions which the somewhat scanty observations seem to justify, and to point out the limitations to which such conclusions are necessarily subject. In general it would seem that the importance to geology of the effects of pressure upon changes such as the melting of a single pure substance—those, namely, usually regarded as physical changes—has been overestimated relatively to that of the influence of pressure upon systems containing more than one component—namely, upon chemical changes. The influence of pressure upon chemical equilibrium is especially marked if one or more of the components of the system are volatile, and must therefore be taken into account in any discussion of the behavior of the magma; indeed, the order of separation from a complex solution containing a volatile component depends just as much on whether, and how, the pressure changes as upon the mode and rate of cooling.

There has been very little direct experiment on the influence of pressure upon the formation of rocks and minerals, by reason of the technical difficulties in the way of making such experiments; so that we are forced in large part to reason from analogy with those substances whose behavior it has been possible to investigate. In reasoning from analogy we must, of course, bear in mind the inherent limitations to which conclusions thus derived are subject. On the other hand, in reasoning backward from present-day field evidence, one must also proceed with caution; for, presuming even that one is aware of all the factors in the net result as we see it, it is hard to disentangle the effects of these several factors, especially since the intensity of each is in general unknown. For example, we can make only a very rough guess at the temperature and pressure prevailing at the time when a given process was taking place, and consequently cannot gauge satisfactorily the relative importance of these factors in producing the result as we see it. Moreover, the

composition of a rock mass as we see it now is no absolute criterion of what was the total composition of the magmatic solution from which it separated; for we are ignorant of the character and amount of the volatile components which were present in the original liquid magma.

In discussing metamorphic processes—or indeed in any discussion of the effects producible by pressure—one must remember to distinguish carefully between uniform (or pure hydrostatic) pressure and non-uniform compression, which is equivalent to a stress; for the former is incompetent to produce some of the results which may be brought about by the latter. This distinction is important; failure to observe it has led to many apparently contradictory statements, and consequently to some confusion. The main difference is that whereas a homogeneous solid body recovers its original dimensions and properties when relieved from a uniform pressure, it is changed permanently by a stress, provided that the stress exceeds the elastic limit of the solid; this residual effect is evident as a change of shape—a deformation—which is accompanied by a change in several other properties, e.g., in the case of metals by changes in density, electric resistance, and thermoelectric power. That the effects of stress on a crystalline aggregate outweigh those of uniform pressure follows from thermodynamical principles if we identify a deformation under stress with a real, partial, local temporary melting, on the basis that the stress acts upon the solid but not upon the liquid phase.¹ This hypothesis, which is not in conflict with any direct experimental evidence, serves to correlate a number of observations on the flow of rocks and of metals, and has in recent years been utilized by several English metallographers as a means of accounting for phenomena connected with the important question of the hardening of metals. In this connection it may be pointed out that the circumstance that a solid has been deformed indicates, not that its strength was necessarily small, but that the shearing forces to which it was exposed were great enough to overcome the resistance to deformation offered by the solid; in other

¹ This hypothesis, and some of its consequences, have been discussed in previous papers; see Johnston and Adams, *Am. Jour. Sci.*, XXXV (1913), 206; Johnston and Niggli, *Jour. Geol.*, XXI (1913), 599.

words, the fact that a rock has flowed is no criterion of its strength, nor does it indicate that at the time of flow the rock was necessarily liquid as a whole.

Let us now consider briefly the effects of uniform pressure upon some of the properties of a pure crystalline substance, taking up first its melting-curve. For a pure crystalline substance there is, at a definite pressure, a single temperature—the melting-point—at which its solid and liquid forms can coexist indefinitely in equilibrium, this being the temperature at which the vapor pressure of solid and that of the liquid become identical. The melting-point is influenced by change of uniform pressure—such as we may conceive to be exerted by either a gas or a mobile liquid (e.g., oil) which is insoluble in the substance. By joining up the melting-points at various pressures we obtain the melting-curve, the slope of which (dT/dP) at any point can easily be shown to be

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

where T , ΔV , and ΔH are respectively the melting-point, the change of volume, and the heat change (latent heat of fusion) at that particular point on the curve. From this equation it is obvious that the general shape of the curve is determined by the way in which ΔV and ΔH vary with the pressure; that the condition for a maximum melting-point is that ΔV should vanish while ΔH remains finite, and for a critical end-point solid-liquid that ΔV and ΔH should vanish simultaneously. But we cannot predict from theoretical principles how ΔH and ΔV will vary—in other words, the shape of the curve can be determined only by experiment. In this connection it may be noted that there is no general relation between ΔH and ΔV , for we may have a large latent heat associated with a small volume change and vice versa; indeed, in two particular cases we have a negative volume change with a positive heat effect, these two exceptional cases—ice I and bismuth—being the only pure substances whose melting-point is known to be lowered by pressure. There is little doubt that the silicates are normal in this respect, showing a rise of melting-point with increase of uniform pressure, because everything indicates that they expand on melting

—that at the melting-point the volume of the liquid is greater than that of the solid.

The best and most extensive experimental work is that of Bridgman,[†] who determined the melting-curve of a number of substances at pressures up to 12,000 atm.—a pressure corresponding to a depth below the surface of the earth of about 30 miles. Some of his data are presented in Table I, which shows especially the gradual diminution of the effect with each successive pressure increment. Bridgman also made direct measurements of the change of volume on melting (ΔV) throughout his pressure range, and found that it decreases slowly and at a continuously decreasing rate; the shape of the curve suggests that the change of volume would not become zero at any finite pressure. Moreover, by combining his data and using the foregoing equation he calculated ΔH ; it does not tend toward zero at higher pressures, but remains approximately constant, showing if anything a tendency to increase with the pressure. The general conclusion from this work accordingly is that, up to pressures of 12,000 atm. at least, there is no indication of a maximum melting-point, still less of a critical end-point solid-liquid; on the contrary everything indicates that such points, if indeed they exist at all, can occur only at pressures altogether outside the range of possible experiment at the present time.

Table I illustrates another interesting point: namely, that at a pressure of about 5,800 atm. the melting-point of solid CO_2 has reached 31° , the critical temperature of the liquid; at pressures higher than this it sublimates or passes directly into a gas. Consequently it is in this case actually possible to pass directly from a *gas* (not a vapor, for it is above the critical temperature) to crystalline solid merely by change of pressure. This would indicate that application of sufficient pressure would convert even a gas into a solid, and suggests that the existence of any large body of gas deep in the earth is as little likely as the existence of much liquid.

All of this evidence then tends to corroborate the belief that the central portion of the earth is substantially solid, though this does not imply that this solid will not flow whenever opportunity

[†] P. W. Bridgman, *Proc. Am. Acad.*, XLVII (1911-12), 347; *ibid.*, XLVII (1911-12), 439; *Physic. Rev.*, III (1914), 126, 153.

occurs for it to do so, since the stresses to which it is exposed must be far in excess of its elastic limit, even at moderate depths.

TABLE I
MELTING-CURVES OF VARIOUS SUBSTANCES (AFTER BRIDGMAN)

| PRESSURE KG. PER SQ. CM.* | MERCURY | | POTASSIUM | | SODIUM | | NITROBENZOL | | CARBON DIOXIDE | |
|---------------------------------|----------|------------|-----------|------------|----------|------------|-------------|------------|-------------------|------------|
| <i>P</i> | <i>t</i> | Δt | <i>t</i> | Δt | <i>t</i> | Δt | <i>t</i> | Δt | <i>t</i> | Δt |
| 1 | -38.85 | 5.10 | 62.5 | 16.2 | 97.6 | 8.6 | 5.6 | 21.9 | -56.6 | 19.3 |
| 1,000 | -33.75 | 5.09 | 78.7 | 13.7 | 106.2 | 8.1 | 27.5 | 21.2 | -37.3 | 16.8 |
| 2,000 | -28.66 | 5.09 | 92.4 | 12.3 | 114.3 | 7.6 | 48.7 | 19.9 | -20.5 | 15.2 |
| 3,000 | -23.57 | 5.09 | 104.7 | 11.1 | 121.9 | 7.2 | 68.6 | 18.8 | - 5.3 | 13.8 |
| 4,000 | -18.48 | 5.08 | 115.8 | 10.2 | 129.1 | 6.9 | 87.4 | 17.7 | + 8.5 | 12.7 |
| 5,000 | -13.40 | 5.08 | 126.0 | 9.4 | 136.0 | 6.6 | 105.1 | 16.9 | 21.2 | 11.7 |
| 6,000 | - 8.32 | 5.07 | 135.4 | 8.7 | 142.6 | 6.3 | 122.0 | 16.1 | 32.9 | 11.1 |
| 7,000 | - 3.25 | 5.06 | 144.1 | 8.1 | 148.9 | 6.1 | 138.1 | 15.5 | 44.0 | 10.6 |
| 8,000 | + 1.81 | 5.06 | 152.2 | 7.5 | 155.0 | 5.9 | 153.6 | 15.1 | 54.6 | 10.2 |
| 9,000 | 6.87 | 5.05 | 159.7 | 7.0 | 160.9 | 5.7 | 168.7 | 14.8 | 64.8 | 9.9 |
| 10,000 | 11.92 | 5.04 | 166.7 | 6.6 | 166.6 | 5.4 | 183.5 | 14.5 | 74.7 | 9.6 |
| 11,000 | 16.96 | 5.03 | 173.3 | 6.2 | 172.0 | 5.2 | 198.0 | | 84.3 | 9.3 |
| 12,000 | 21.99 | | 179.5 | | 177.2 | | | | 93.6 | |

* 1 atm. = 1.033 kg. per sq. cm.

As regards the magnitude of the effect of uniform pressure in raising the melting-point of a pure silicate, there are no experimental data; but the initial slope of the melting-curve could be calculated if the latent heat and volume change on melting were known. The relevant evidence is very scanty and unsatisfactory; but, so far as it goes, it indicates that the latent heat is of the order of 100 cal.¹ per gram and that the volume change ranges up to 10

¹ With regard to this estimate see: J. H. L. Vogt, *Die Silikatschmelzlösungen*, II (1904), 65; W. P. White, *Am. Jour. Sci.*, XXVIII (1909), 486 (footnote); G. Mulert, *Z. anorg. Chem.*, LXXV (1912), 238.

per cent,¹ or about 0.04 cc. per gram. On this basis² the rise of melting-point of a *pure* silicate produced by a pressure of 1,000 atm. would range up to 15°, with a possibility of a somewhat greater rise in exceptional cases (specifically, whenever the latent heat is small, unless the change of volume is at the same time very small). Accordingly, the change of melting-point would be of the order of 6° for the first mile in depth, an amount which, in all probability, would with each succeeding mile decrease steadily at a steadily decreasing rate, but would not become zero.

Now the question arises—could the temperature gradient downward overtake the pressure gradient? It would seem that this possibility is not to be excluded, for, according to the best evidence (likewise very scanty), the increase in temperature for one mile in depth is about 40° C.; consequently, if we assume that this gradient and the melting-curve gradient remain constant, the temperature would at a depth of 35 miles be 1,400° C., the approximate temperature at which many pure silicates exposed to the pressure existing at that depth would melt.

The foregoing reasoning applies only to a pure silicate melting to a liquid of its own composition; but to reason from the behavior of a single pure substance to its behavior in contact with a complex solution is of doubtful utility. For in the latter case the relative *solubility* of the substance in the solution under the particular conditions obtaining is the decisive factor which determines whether it shall separate, though of course it will not separate unless it would normally be solid (crystalline) at the prevailing temperature and pressure; and, so far as experience goes, pressure has very little influence on solubility in condensed systems (that is, systems without a vapor phase). The foregoing serves to emphasize the fact that any conclusions as to what will happen to rocks at high temperatures and pressures must still be considered to be subject to very serious limitations.

Reversible transformation points solid \rightleftharpoons solid (that is, enantiotropic inversions) are altogether analogous to melting-points, and

¹ See Day, Sosman, and Hostetter, *Am. Jour. Sci.*, XXXVII (1914), 1; cf. the results cited by R. A. Daly, *Am. Jour. Sci.*, XV (1903), 276.

² $\Delta T = \frac{T\Delta V}{41.3\Delta H} \times \Delta P = \frac{1,500 \times 0.04}{41.3 \times 100} \times 1,000 = 15^\circ$ for 1,000 atm.

consequently the reasoning with regard to the shape of the melting-curve is, *mutatis mutandis*, applicable here; with this difference, however, that a maximum on the transformation curve is possible, since there appears to be no necessity that the solid form stable at the higher temperature should always have the greater specific volume. On the other hand, nothing whatever can be predicted as to the influence of pressure on monotropic (apparently irreversible) transformations, such for example as marcasite→pyrite, or aragonite→calcite; for such inversions take place whenever and wherever their rate becomes appreciable. Consequently the temperature region within which a monotropic inversion takes place varies with the conditions, especially such as the presence of a solvent; but there is no evidence that uniform pressure accelerates such transformations at all.¹ This conclusion is borne out by the fact that high pressure acting on either marcasite or aragonite was absolutely without effect in inducing the transformation to the more stable form. In this connection, however, it is to be remarked that it is possible that an inversion which is monotropic at one pressure may at another pressure be enantiotropic; no actual case of this is known, but this is not surprising in view of the small amount of work hitherto carried out under a wide range of pressures.

Very frequently rise of temperature causes one crystal form to change over into another (e.g., quartz→tridymite→cristobalite); rise of pressure (at constant temperature) in many cases produces a precisely analogous result—in other words, certain modifications are really stable only at high pressure. It follows that investigation of pure substances over a wide pressure range will frequently result in the discovery of hitherto unknown modifications of those substances. A beautiful example of this is the substance water, of which no fewer than five solid modifications are now known;² the relations between these are given in Table II and also in Fig. 1,

¹ The influence of pressure on rate of reaction in condensed systems has been investigated in very few cases: apparently it is very small, and may be either an acceleration or retardation. See E. Cohen and R. B. de Boer, *Z. physik. Chem.*, LXXXIV (1913), 41; E. Cohen and H. F. G. Kaiser, *Ibid.*, LXXXIX (1915), 338.

² P. W. Bridgman, *Proc. Am. Acad.*, XLVII (1912), 439-558; for other examples see Bridgman, *Physic. Rev.*, III (1914), 153-203.

which shows the fields of stability of the several forms and the several melting and transformation curves. From the diagram it is evident that if we keep the temperature constant at -20° , and increase the pressure gradually, the following sequence of events will occur: at 2,000 atm. ice I will melt, but the liquid will freeze again to ice III at 2,500 atm.; this in turn will pass over into ice V at 3,500 atm. which at 6,300 atm. will pass over into ice VI. At any temperature above 0° , no solid would appear until the pressure exceeded 6,400 atm. when ice VI would appear at a pressure depending on the temperature, e.g., 20,000 atm. at $+73^{\circ}$.

TABLE II

NUMERICAL DATA PERTAINING TO THE EQUILIBRIUM DIAGRAM FOR WATER—
LIQUID AND FIVE SOLID FORMS* (AFTER BRIDGMAN)

| Pressure kg. per sq. cm. | Corresponding Temperature | Phases in Equilibrium |
|--------------------------|---------------------------|--|
| I. | 0.0 | Freezing-point: ice I-liquid |
| 1,000. | - 8.8 | " " " " |
| 2,000. | -20.15 | " " " " |
| 2,115. | -22.0 | Triple point (A): ice I-ice III-liquid |
| 2,170. | -34.7 | " " (B): " " -ice II |
| 3,510. | -24.3 | " " (C): ice III-ice V-ice II |
| 3,530. | -17.0 | " " (D): " " -liquid |
| 4,500. | -10.2 | Freezing-point: ice V-liquid |
| 5,500. | - 4.2 | " " " " |
| 6,380. | + 0.16 | Triple point (E): ice V-ice VI-liquid |
| 8,000. | +12.8 | Freezing-point: ice VI-liquid |
| 12,000. | +37.9 | " " " " |
| 16,000. | +57.2 | " " " " |
| 20,000. | +73.6 | " " " " |

* The notation ice IV was not used, as it had already been assigned by Tammann to another reputed form, which differs little from ordinary ice (I); the existence of this form, which was not encountered by Bridgman, is very doubtful.

Nor must it be supposed that the foregoing example is exceptional; indeed, it is now certain that polymorphism—i.e., the ability of a single chemical substance to appear in more than one crystalline form—is of frequent occurrence, even without the intervention of change of pressure. For example, sulphur exists in at least four forms, silica in at least six forms, etc. Now the form stable under high pressure may persist at ordinary pressure, just as high-temperature forms may persist at ordinary temperature; we may expect, therefore, that extended pressure investigations

will yield substances hitherto unobtained or even unknown, some of which might prove to be of technical importance. An illustration of this is the new form of phosphorus recently discovered by Bridgman;¹ this form is grayish black like graphite, has a high density (2.69, as against 2.34 for the red variety and 1.9 for the yellow), is ignited with difficulty by a match, and cannot be exploded by a blow from a hammer, as red phosphorus can. Never-

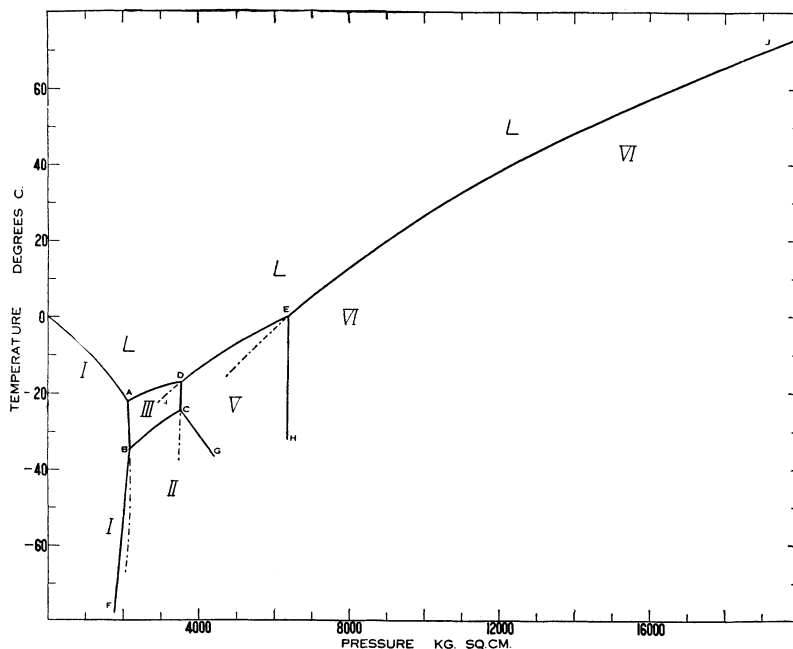


FIG. 1.—Equilibrium diagram for water—liquid and five solid forms

theless it is probable that uniform pressure has been essential to the formation of but few ordinary minerals, except in so far as it was effective in securing an adequate concentration of some volatile component (or components) in the magma from which the minerals separated.

So far we have taken up the effects of pressure upon a single pure substance; when we deal with systems of more than one

¹ P. W. Bridgman, *Physic. Rev.* III (1914), 187.

component, the mutual solubilities¹ enter as factors in the result. These are affected by pressure because it changes the relative concentrations or activities of the several components. This influence is slight with solids and liquids, because their compressibilities are very small; but in systems with a gaseous phase it is very great, because the concentration of a gas is directly proportional to the pressure, so that in such systems change of pressure will have a marked influence on the relative concentrations of the several reacting components.

In accordance with this, the influence of uniform pressure upon solubility and upon chemical equilibrium in condensed systems—that is, systems in which there is no vapor phase—is slight, and for practical purposes negligible in comparison with the influence of temperature or change of composition of the solution. Thus the few trustworthy experiments made hitherto show that a pressure of 1,000 atm. changes the solubility of a salt in water by only about 1 per cent of its value—a change which may readily follow a temperature change of a few degrees or a slight change of composition of the solution.² Again, at ordinary temperatures the liquids water and methylethylketone are only partially miscible at 1 atm., but they become completely miscible at about 1,100 atm.,³ whereas at 1 atm. this does not take place until a temperature of 152° is reached. The opposite effect—i.e., unmixing by increase of pressure—could equally well be produced, just as it may be by increase of temperature. But it seems probable that neither of these effects is of importance in liquid mixtures of silicates, because liquids which

¹ It is to be remembered that mutual solubilities can be altered by the addition of a third component, even though it forms no part of the solid phase which separates. Thus, as is evident from fig. 6 of Rankin's paper (*Am. Jour. Sci.*, XXXIX [1915], 1-78), a mixture composed of 60 per cent SiO₂, 40 per cent Al₂O₃, on cooling deposits Al₂SiO₅ (sillimanite), whereas in presence of CaO, in amount ranging from 3 to 30 per cent of the whole, the solid phase which separates is *pure* Al₂O₃. This illustrates how even a small change in composition of a solution may alter the course of crystallization.

² E. Cohen and L. R. Sinnige, *Z. physik. Chem.*, LXVII (1909), 432; LXIX (1909), 102; E. Cohen, K. Inouye, and C. Euwen, *ibid.*, LXXV (1911), 257. These authors give a critical résumé of earlier work along this line.

³ P. Kohnstamm and J. Timmermanns, *Proc. K. Akad. Wetenschappen*, XV (1913), 1021-37.

are so much alike chemically as are the silicates are usually completely miscible under all conditions.

But the effect is of another order of magnitude in presence of a gas phase which may enter into reaction or solution with other components; and consequently this circumstance must be taken into consideration in any discussion of the behavior of the magma, which undoubtedly contains volatile components of this character.

TABLE III

THE SOLUBILITY* OF CaCO_3 AT 16° AND ITS DEPENDENCE UPON THE PARTIAL PRESSURE OF CO_2 OVER THE SOLUTION

| Partial Pressure of CO_2 in Atmospheres | Solubility Parts CaCO_3 per Million Parts Water |
|---|--|
| 0.0 | 14.3 |
| 0.00037 | 46.1 |
| 0.00050 | 74.6 |
| 0.0033 | 137.2 |
| 0.0139 | 223.1 |
| 0.0282 | 296.5 |
| 0.0501 | 360.0 |
| 0.142 | 533.0 |
| 0.254 | 663.0 |
| 0.417 | 787.0 |
| 0.553 | 885.0 |
| 0.730 | 972.0 |
| 0.984 | 1,086.0 |

* Data according to Schloesing (*Compt. rend.*, LXXIV [1872], 1552; LXXV [1872], 70, except the first two, which are due to Kendall [*Phil. Mag.*, XXIII (1912), 958-76]).

As a simple example, consider the amount of CaCO_3 which will dissolve in water inclosed in a vessel with various partial pressures of CO_2 . In pure water it is 14 parts per million, an amount which is trebled by the presence of as little as 0.00037 atm. CO_2 (3.7 parts in 10,000, about the proportion of CO_2 in ordinary air) and has increased by more than 70 times when the CO_2 pressure reaches 1 atm. (see Table III). This great increase is an example of the very great effect of increase of concentration (partial pressure) of a gaseous component; it is, of course, due to the formation of calcium bicarbonate in the solution, but this circumstance in no wise affects the force of the argument. Indeed, this is an excellent illustration

of the law of mass action, as the calculations made by Stieglitz show.¹

A closely related point is that a compound resulting from a reaction involving a volatile component will not be formed unless the concentration—in other words, the partial pressure—of that component is above a certain limiting value, this value being dependent on the conditions, on the temperature especially. An illustration may serve to make this clearer. If we wish to keep liquid water at 200° we must have it in a closed vessel capable of withstanding the vapor pressure of water at that temperature, which amounts to about 15 atm. (225 lbs per sq. inch); likewise at 300° the vessel would require to be strong enough to support an internal pressure of 100 atm.; but if the vessel should leak, either because it was not strong enough or because it was not tightly closed, the vapor would escape and the liquid water would disappear. Similarly we can keep Ca(OH)_2 as hydroxide at 550° in steam at 1 atm., but at 750° it would be necessary to have a pressure of water vapor of about 15 atm. (and at 950°, about 100 atm.) if we wish to retain it all as hydroxide and to have no oxide present; in other words, if we should wish to prepare Ca(OH)_2 from CaO at a temperature of 750°, we could do so only by having continuously a pressure of at least 15 atm. of water vapor above it.

It may happen, therefore, that the product which actually separates in certain cases will be determined by the magnitude of the pressure of water vapor at the time of separation. This serves to account for the fact that the biotite of many deep-seated igneous rocks is replaced in their effusive forms by olivine and leucite (which are in the aggregate chemically equivalent to biotite from which water has escaped)—a relation which has been brought out by Iddings, Bäckstrom, and others. Similarly, muscovite is found only in granitic rocks consolidated at depth, while in their surface equivalents the water has in part escaped and the potash has entered feldspar and biotite.

¹ J. Stieglitz, "The Relations of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulphate, Calcium Carbonate, and Calcium Bicarbonate of Water Solutions in Contact with It," *Carnegie Institution of Washington, Publication No. 107* (1909) (*The Tidal and Other Problems*, by T. C. Chamberlin *et al.*), pp. 235-64.

A noteworthy point in this connection is that water vapor—or, for that matter, any volatile component—may, and does, act in a way precisely analogous to any non-volatile component, the only difference being that it in general requires pressure in order to hold it on the job, so to speak. As an illustration, let us consider the equilibrium diagrams in Fig. 2, I for the system $\text{LiNO}_3\text{--KNO}_3$, II for the system $\text{H}_2\text{O--KNO}_3$, III for the system $\text{H}_2\text{O--CrO}_3$. In I, L is the melting-point of pure LiNO_3 , which by admixture of KNO_3 is lowered along the line LE : this line therefore represents the equilibrium between solid LiNO_3 and liquid mixtures of LiNO_3 and KNO_3 of various compositions; in other words, it is the solubility curve of LiNO_3 in these mixtures. Similarly KE represents the equilibrium between solid KNO_3 and liquid. These two curves meet in E , the so-called eutectic point, at which point (132°) a liquid of the composition 45 per cent LiNO_3 , 55 per cent KNO_3 freezes to an agglomerate of the same composition. In II, point I is the freezing-point of water, and IC the freezing-point of solutions of KNO_3 ; in other words, IC is the equilibrium line along which ice is in equilibrium with mixtures of H_2O and KNO_3 of various compositions. The line KC represents the equilibrium between solid KNO_3 and mixtures of KNO_3 and H_2O ; the end nearer C is the ordinary solubility curve of KNO_3 in water, while toward K it would be more logically called the solubility curve of H_2O in KNO_3 . The curves meet in C , which in the case of aqueous solutions is usually called the cryohydric point. These two systems are thus obviously altogether similar, the sole difference resulting from the difference in the vapor pressures of H_2O and LiNO_3 in relation to the prevailing atmospheric pressure; namely, that whereas at the temperatures concerned the vapor pressure of LiNO_3 is inappreciable, that of water ranges from some millimeters up to many atmospheres. The equilibrium curve (III, Fig. 2) for the system $\text{H}_2\text{O--CrO}_3$ is included because in form it resembles very closely that for $\text{LiNO}_3\text{--KNO}_3$; the branch of the curve on the water side is much longer than in the case of $\text{H}_2\text{O--KNO}_3$, corresponding to the much greater solubility of CrO_3 in water at and below 0° .

At each point on the curve CK the liquid in equilibrium with solid KNO_3 has a definite composition and therefore a definite vapor

pressure of water which must be maintained in order to secure the appropriate concentration. This vapor pressure becomes equal to 1 atm. at about 120° (the ordinary boiling-point of a saturated aqueous solution of KNO_3); increases, as we ascend the curve, to a maximum, which in this case is only 2 or 3 atm., and finally decreases to zero at the point *K*. In systems such as this—namely, in which the liquid may have (under the appropriate conditions)

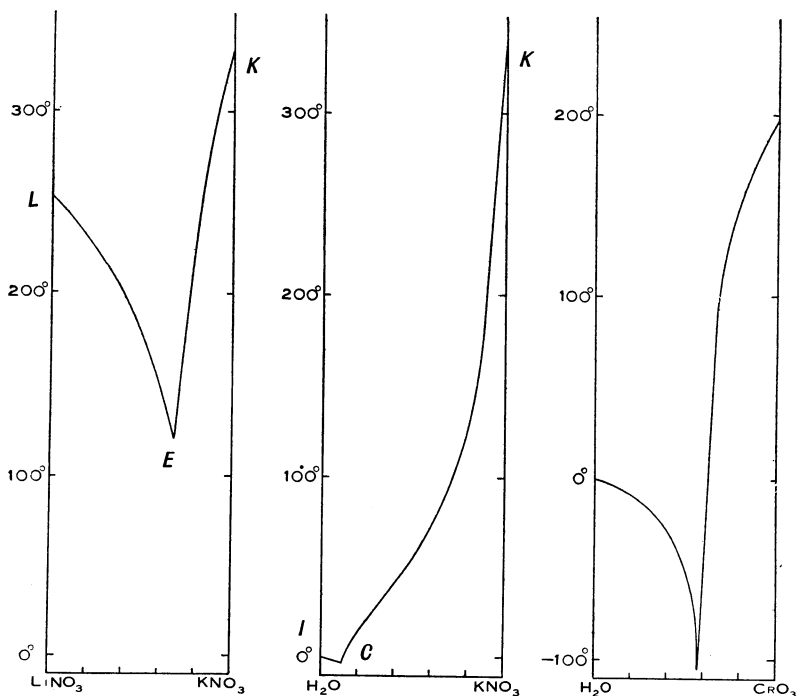


FIG. 2.—To show the similarity between the equilibrium diagrams of the system $\text{LiNO}_3\text{--KNO}_3$, $\text{H}_2\text{O--KNO}_3$, $\text{H}_2\text{O--CrO}_3$.

any composition ranging from one pure component to the other—the magnitude of the maximum equilibrium pressure depends mainly on the melting-point of the salt; where the melting-point is low, as for KOH , the maximum pressure is less than 1 atm.; where it is high, as for potassium silicate, the maximum is some hundreds of atmospheres. Nevertheless, as is evident from the diagram, the lowering of melting-point produced by a comparatively

small amount of water may be quite large; for it would seem that a lowering of 100° could easily result from the presence of water vapor at a pressure less than 20 atm. Incidentally it may be pointed out that the circumstance that pure water has a critical point at 370° and 200 atm. is of secondary importance in the discussion of systems belonging to this type.¹

The great similarity exhibited by these two systems shows that there is no real difference between melting-curves and solubility curves; a simple and well-known illustration of this is the fact that the melting-point of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to a liquid of its own composition is merely a particular point on the graph representing the solubility of CaCl_2 in water. In general it is much simpler to consider all such phase diagrams as solubility diagrams, as by so doing it is easier to grasp their full significance and to predicate what will happen under specified circumstances. This point was clearly stated thirty years ago by Guthrie, the first investigator of eutectics, who wrote as follows:²

[My experiments show] that water at a high temperature may not only play the part of a solvent in the ordinary restricted sense, but that there is in many cases no limit to its solvent faculty; in other words, that it may be miscible with certain rocks in all proportions: that solution and mixture are continuous with one another. And this continuity, as my experiments prove, is established in some cases—and these indeed with bodies having no chemical affinity with water—at temperatures not above the temperatures of fusion of those bodies *per se*.

Moreover, Guthrie saw the geological significance of these results, for he wrote:

Just as in the selective formation of salt-alloys we may have the artificial type of the genesis of many primary rocks and metamorphic modifications, so in the wonderful solubility in or miscibility with water of such alloys and of some salts at high temperatures we may have a no less clear type of the formation of certain volcanic rocks and an explanation of some of their peculiarities. . . . Obsidian melted and under pressure will, I presume, mix freely with water. When this pressure is gradually removed, water vapor escapes, and although it takes with it a large amount of heat, the temperature of the obsidian

¹ With regard to this point see Morey and Niggli, *Jour. Am. Chem. Soc.*, XXXV (1913), 1089 ff.

² *Phil. Mag.*, XVIII (1884), 117.

may still remain above its point of anhydrous fusion, or it may be maintained fused by heat from other sources. Finally cooled, it is the familiar glassy amorphous mineral. A quick release of pressure entails a quick vaporization of water and a quick loss of heat. The obsidian mass, during and because of the loss of water and the loss of heat, becomes pasty and "rises" like dough during fermentation, and becomes pumice, which is often found overlying obsidian. A quicker release of pressure from above causes the vesicular and vesiculating masses to be projected, and if the vesiculation is carried far and fast, volcanic dust is produced.

The phenomena discussed in the paragraph just quoted have now been realized experimentally with potassium silicates by Morey, who was able to produce at will either a hard or a pumiceous glass merely by altering the mode of cooling.¹

What has been said about systems containing volatile components may be applied to elucidate some aspects of the behavior of a cooling magma. If the crystals separating out initially from a magma situated within a confined space contain none of the volatile component, then the concentration of the volatile component in the residue would become continuously greater, and consequently the vapor pressure would *increase*; this increase might under certain circumstances be large, so that there would be a considerable tendency to enlarge the space within which the magma is confined. Accordingly eruption of a magma may be correlated with a comparatively early stage of its crystallization. On the other hand, the initiation of crystallization may be due to the circumstance that the pressure was relieved—by faulting in the adjacent rock, or otherwise—whereupon the magma began to lose its volatile components, and consequently to crystallize; this process is precisely analogous to the crystallization of a salt from a solution by boiling off the solvent.

If no escape is possible, the residue from the crystallization of the main portion of the non-volatile constituents will be a *fluid* (as distinct from a liquid) solution, containing silicates and probably sulphides, etc., which is so mobile that it can easily penetrate the adjacent rock, producing the phenomena of contact metamorphism and injection. Thus we can account for the very thin veins and dikelets often observed at igneous contacts, which indicate that at

¹ G. W. Morey, *Jour. Am. Chem. Soc.*, XXXVI (1914), 226-27.

some period the rock was permeated by very mobile solutions from which crystals subsequently separated while the still volatile components passed on. It was presumably in some such way that the pegmatites formed, for there are other reasons for believing that they formed at about 600° , a temperature at which all their constituent minerals would long have been solid had there been no volatile components present.

SUMMARY

In the foregoing pages is presented a brief discussion of some aspects of the influence of pressure on the formation of rocks and minerals. In general it would seem that the importance to geology of the effects of pressure upon so-called physical changes (e.g., the melting-point of a single pure substance) has been overestimated relatively to that of the influence of pressure upon chemical changes—in other words, upon equilibrium in polycomponent systems. Change of effective pressure will in general change the configuration of the various fields of stability in a system, acting thus in a way precisely analogous to change of temperature, or of gross composition; but in the case of pressure the effect will usually not be especially marked unless one or more of the components is volatile—that is, unless the concentration of one or more of the components really changes appreciably with change of pressure. This is merely an example of the general rule that the magnitude of the effect of pressure on a system depends upon the difference in compressibility of the several phases present, being greatest when this difference is greatest, and conversely.

Accordingly we must, in any discussion of the course of crystallization from a complex magmatic system, take into account the mode in which the effective pressure varies as well as the mode of cooling. For change of pressure, like change of temperature, may affect the order of crystallization—and even the character—of the minerals which separate; this result of course depending merely upon the circumstance that the saturation limits (solubilities) of the several solid phases which could possibly separate out are not all affected equally by change of conditions.